of an alkaline earth metal, Sc, Ti, V, Cr, Y, Zr, Nb, Hf, Ta, W, a rare earth metal, and their nitrides, amides, imides, amido-imides, or halides.

In some embodiments, at least one of the mineralizer and the getter are placed in crucibles within or proximate to the raw material basket.

The use of metallic precursors for the raw material, mineralizer, and/or getter is convenient in some respects. For example, the metal is typically available commercially in high purity, and no further synthesis is required. However, in addition to the complexity of suitably supporting a metal that melts under reaction conditions (e.g., Ga, Na, K), the use of a pure metal may generate undesirable gases, such as hydrogen. For example, under ammonthermal reaction conditions the metals listed below will undergo one or more of the following reactions:

$$Ga+NH_3=GaN+3/2H_2$$

$$Na+NH_3=NaNH_2+\tfrac{1}{2}H_2$$

$$K+NH_3=KNH_2+\tfrac{1}{2}H_2$$

$$Mg+2NH_3=Mg(NH_2)_2+H_2$$

$$3Mg+2NH_3=Mg_3N_2+3H_2$$

$$Y+3NH_3=Y(NH_2)_3+3/2H_2$$

$$Y+NH_3=YN+3/2H_2$$

The presence of hydrogen in the supercritical fluid solvent may decrease the solubility of gallium-containing species and, further, may embrittle the metal constituting the autoclave walls.

The use of azides as mineralizers is convenient in that they are often available commercially in high purity, can be purified further, and are considerably less hygroscopic than the alkali metals or amides or the alkaline earth nitrides, for example. Use of azide mineralizers is suggested by Dwiliński in U.S. Pat. No. 7,364,619, which is hereby incorporated by reference in its entirety. However, azides typically decompose under reaction conditions, generating undesirable gases, such as nitrogen:

$$3NaN_3+2NH_3=3NaNH_2+4N_2$$

In a preferred embodiment, these two effects are combined so as to cancel each other out. Metals, including raw materials, mineralizers, and getters, are added together with azide mineralizer precursors such that H_2 and N_2 are generated in approximately a 3:1 ratio. The reaction container further comprises means for catalyzing NH_3 formation from H_2 and N_2. Catalysis of the reaction between H_2 and N_2 liberated in the reaction of the metal with ammonia and decomposition of the azide, respectively, to re-form ammonia may be performed by the autoclave walls or by added catalyst. The added catalyst may comprise powder, granules, foil, a coating, bulk material, or a porous pellet. The added catalyst may comprise at least one of iron, cobalt, nickel, titanium, molybdenum, tungsten, aluminum, potassium, cesium, calcium, magnesium, barium, zirconium, osmium, uranium or a lanthanide, ruthenium, platinum, palladium, or rhodium. For example, a mole of added NaN_3 will generate 4/3 mole of N_2. The latter can be counterbalanced by also adding 8/3 moles of Ga metal, which will generate 8/3×3/2 mole=4 moles of H_2, viz., three times the number of moles of N_2 from NaN_3.

The sealable container is then closed and sealed except for a connection to a gas, liquid, or vacuum manifold. In one embodiment, the high pressure apparatus comprises an autoclave, as described by U.S. Pat. No. 7,335,262, which is hereby incorporated by reference in its entirety. In another embodiment, the sealable container comprises a metal can, as discussed by U.S. Pat. No. 7,125,453, a container, as discussed by U.S. Patent Application No. 2007/0234946, or a capsule, as discussed by U.S. patent application Ser. No. 12/133,365, entitled "Improved capsule for high pressure processing and method of use for supercritical fluids," all of which are hereby incorporated by reference in their entirety. The inner diameter of the autoclave or capsule may be between 1 inch and 2 inches, between 2 inches and 3 inches, between 3 inches and 4 inches, between 4 inches and 6 inches, between 6 inches and 8 inches, between 8 inches and 10 inches, between 10 inches and 12 inches, between 12 inches and 16 inches, between 16 inches and 24 inches, or greater than 24 inches. The clearance between the inner diameter of the autoclave or capsule and the outer diameter of the frame may be between 0.005 inch and 1 inch, or between 0.010 inch and 0.25 inch. The ratio of the inner height of the autoclave or capsule to its inner diameter may be between 1 and 2, between 2 and 4, between 4 and 6, between 6 and 8, between 8 and 10, between 10 and 12, between 12 and 15, between 15 and 20, or greater than 20.

After slicing, the crystal wafers may be lapped, polished, and chemical-mechanically polished by methods that are known in the art.

In a specific embodiment, any of the above sequence of steps provides a method according to an embodiment of the present invention. In a specific embodiment, the present invention provides a method and resulting crystalline material provided by a pressure apparatus having a basket structure. Other alternatives can also be provided where steps are added, one or more steps are removed, or one or more steps are provided in a different sequence without departing from the scope of the claims herein.

While the above is a full description of the specific embodiments, various modifications, alternative constructions and equivalents may be used. Therefore, the above description and illustrations should not be taken as limiting the scope of the present invention which is defined by the appended claims.

What is claimed is:

1. A process for growing a crystalline gallium-containing nitride, the process comprising:

providing a high pressure apparatus comprising gallium-containing feedstock in one zone, at least one seed in another zone, an azide mineralizer, and at least one metal, the azide mineralizer and the metal being provided in a predetermined ratio such that nitrogen generated by decomposition of the azide mineralizer and hydrogen generated by reaction of the metal with a supercritical fluid are in a ratio of approximately 1:3;

processing one or more portions of the gallium-containing feedstock in the supercritical fluid to provide a supercritical solution comprising at least gallium containing species at a first temperature; and

growing crystalline gallium-containing nitride material from the supercritical solution on the seed at a second temperature, the second temperature being characterized to cause the gallium containing species to form the crystalline gallium containing nitride material on the seed.

2. The process of claim **1**, further comprising providing a catalyst in a vicinity of at least one zone or the other zone of the high pressure apparatus to convert the nitrogen and hydrogen to ammonia.